



Surface structure and high-rate performance of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated with N-doped carbon as anode material for lithium-ion batteries



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HIGHLIGHTS

- Individual N and C sources are applied to coat N-doped carbon layer on $\text{Li}_4\text{Ti}_5\text{O}_{12}$.
- This straightforward methodology is easy to optimize N/C ratio and carbon layer thickness.
- The N-doped C-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ presents uniform or serrated surface structure.
- Surface modified samples display outstanding electrochemical properties at high current rate.

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ABSTRACT

We have reported a straightforward strategy to fabricate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composites coated with N-doped carbon layer by using NH_3 as N source and sugar as C source, which is a benefit for optimizing carbon layer thickness and tuning atomic ratio of N/C. The composite was synthesized by a conventional solid state reaction with ball milled mixture of TiO_2 , Li_2CO_3 , and sugar as the precursor, then followed by a high temperature annealing in the atmosphere of Ar and NH_3 . The choice of titanium source has an impact on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ surface morphology as well as electrochemical properties. N-doped TiO_2 can lead to the generation of uniform N-doped C-coating layer, resulting in improved electrochemical performances at high current rate. The N-doped C-coating $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained by using Anatase TiO_2 produces a serrated thin carbon layer, showing the best electrochemical behaviors with the discharge capacity of 100 mAh g^{-1} at high rate of 24 C and 92.2% of initial capacity after 800 cycles at 12 C, which should be one of the promising anode materials for hybrid electric vehicles.

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1. Introduction

Three traditional energies including coal, oil and natural gas, soon are running out, which have brought about global warming and ecological environmental degradation [1,2]. Exploring renewable energy materials has become one of the most important trends all over the world. In recent years, rechargeable lithium ion batteries (LIBs) have attracted worldwide attention for the outstanding advantages such as high safety, high power density, long cycle life, fast charge/discharge properties and friendliness to the environment [3]. As a result, it is gradually becoming one of the most popular electrochemical energy storage devices to save those petrified energy sources and decrease the environmental burden. However, graphite used as a conventional anode in commercial LIBs displays quite slow Li^+ diffusion at low temperature, which results

in serious kinetic problem under the condition of high rate charge/discharge [4]. In addition, Li^+ insertion/deinsertion potential of the graphite anode is below 0.2 V vs. Li/Li^+ , which is near metallic lithium deposition potential, rendering the great possibility of internal electrical short for the batteries.

As an alternative to graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode material has many promising characteristics, such as a relatively high potential plateau at about 1.55 V vs. Li/Li^+ for avoiding the formation of solid state interphase (SEI) layer, a zero-strain insertion material for providing excellent long cycle life [3,5], the unique thermodynamic stability for promoting the safety [6]. All of these merits make LTO particularly attractive as the advanced anode material of high power LIBs for large-scale application. Nevertheless, the pretty low electronic conductivity (merely $10^{-13} \text{ S cm}^{-1}$) leads to serious electrochemical polarization at high current densities [7,8]. So far, various strategies have been proposed to resolve the issue of poor electronic conductivity and lessen the polarization, which

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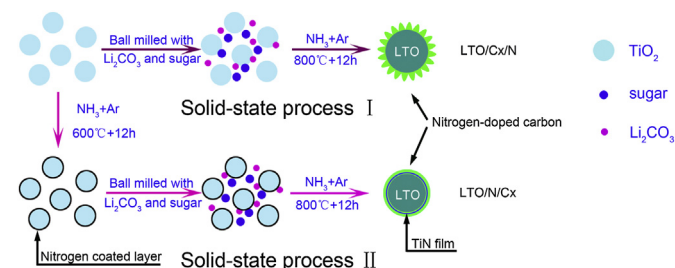
include reducing the particle size down to deca-nanometer scale by soft chemical methods (sol–gel, solvothermal synthesis, spray-drying, etc.) [9–12], doping with foreign metal or non-metal ions (Zn^{2+} , La^{3+} , Nb^{5+} , Mo^{6+} , Mg^{2+} , Ni^{3+} , Al^{3+} , Cr^{3+} , C_0^{3+} , Mn^{3+} , V^{5+} , F^- , Cl^- and Br^-) [7,13–18] and coating excellent electronic conductive matters (Ag, amorphous carbon, graphite and graphene) [19–21] on the surface. Among various methods, the well-known surface carbon-coating technique is one of the most effective ways to improve the rate performance of the electrode material. For instance, G. N. Zhu prepared carbon-coated (C-coated) LTO nanoporous microspheres by a spray drying method combined with high temperature annealing, and the corresponding discharge capacity is up to 126 mAh g^{-1} at a high current rate of 20C [20]. However, the simple C-coated LTO cannot satisfy the requirements of the practical application considering either high rate electrochemical performance or volume energy density because of the difficulty in enhancing electrical conductivity of the coated carbon film itself, forming a defect-free coating layer, etc. To overcome these crucial issues, some researchers have reported a new surface coating technique using the precursor containing carbon and nitrogen elements to deposit a very thin film on the LTO surface. The nitrogen-doped (N-doped) carbon forms a perfect consecutive electronic conductive layer, and effectively improves the rate performance. Recently, Y.S. Hu has proposed several organic species where one material contains at least carbon and nitrogen elements, namely pyridine [22], ionic liquids [23] and urea [24], as N-doped carbon precursor, which greatly enhanced the surface electrical conductivity and optimized the electrical contact within the electrode.

In the work reported here, we developed a simple method to coat N-doped carbon layer on LTO particles, where C and N elements were independently from different precursors. Sugar was applied as C source [25], which is mixed with TiO_2 and Li_2CO_3 for a solid-state reaction. Different from conventional carbon coating process, the high temperature annealing was done in the atmosphere of NH_3 [26], resulting in the formation of N-doped carbon layer. This straightforward methodology had the advantage to easily optimize the ratio of N/C and the carbon layer thickness. Furthermore, we found the surface state of TiO_2 precursor played an important role in the quality of the coated carbon layer.

2. Experimental

2.1. Material preparation

All the chemicals were of analytical grade. The spinel LTO was synthesized via a simple solid state reaction, which is easy to be scale-up for industrial production. In terms of the type of titanium source, the synthesis methodologies were classified as solid-state processes I and II, as shown in Scheme 1. As for solid-state process I, anatase TiO_2 as titanium source and Li_2CO_3 as lithium source



Scheme 1. Schematic illustration for the synthesis of the LTO/C20/N and LTO/N/C20 compounds.

were firstly weighted with Li:Ti molar ratio of 4:5. Secondly, the mixture was ball milled with sugar as carbon source while sugar:TiO₂ weight ratio was varied from 10:100, 20:100 to 30:100. Finally, the well-milled precursor was annealed at 800 °C for 12 h in the mixed atmosphere of Ar and HN_3 , in which $\text{NH}_3 \cdot \text{H}_2\text{O}$ was applied as nitrogen source. The obtained samples were labeled as LTO/C_x/N ($x = 10, 20$, and 30), respectively. The solid-state process II was same as solid-state process I, except that TiO_2 raw material was pre-treated under 600 °C for 3 h in a mixed atmosphere of Ar and HN_3 so as to form N-doped TiO_2 . Correspondently, the synthesized final products were labeled as LTO/N/C_x ($x = 10, 20$, and 30).

2.2. Material characterization

The crystalline phases of LTO composites were identified by X-ray diffraction using $\text{Co K}\alpha$ radiation (XRD, $\lambda = 1.7890 \text{ \AA}$, X'Pert Pro MPD) with a step size of 0.03° (2θ) in the range of $18\text{--}85^\circ$. The morphologies of the samples were observed using a field-emission scanning electron microscope (FE-SEM, Hitachi, S3400N) and transmission electron microscope (TEM, JEOL, JEM-100CX). The lattice images were collected with a high-resolution transmission electron microscope (HR-TEM, FEI, Tecnai F20). The components of the coated layers were analyzed with a Fourier Transform Infrared Spectrometer system (IR, IRrestige-21).

2.3. Cell assembling and electrochemical test

The electrochemical properties of the active materials were measured by assembling half cells. The LTO working electrode was prepared by casting N-methyl-2-pyrrolidone (NMP) slurry onto a Cu foil with the active material, carbon black as conducting additive and polyvinylidene fluoride (PVDF) as the binder at a weight ratio of 8:1:1. Subsequently, the electrode was dried under vacuum at 110°C for 24 h. The test cell was assembled in an Ar filled glove-box using lithium metal foil and polypropylene (PP) membrane (Celgard 2400) as the counter electrode and the separator, respectively. And the electrolyte was 1 mol L^{-1} LiPF_6 dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) (1:1:1 by volume). The charge/discharge measurements were carried out under desired current densities with the voltage between 1.0 and 3.0 V by using a CT2001A cell test instrument (LAND Electronic Co.) at room temperature. Cyclic voltammograms (CV) were performed from 1.0 to 3.0 V at different scanning rates using Solartron SI1287.

3. Results and discussion

Fig. 1 shows XRD curves of all of LTO based products. As the references, pristine LTO and N-doped LTO and C-coated LTO were synthesized, and the corresponding XRD patterns were shown in Fig. 1a and Fig. 1b. It is apparent that the most intense diffraction peaks appear at 21.5 , 41.7 , 50.7 and 74.5° , which are indexed to (111), (311), (400) and (440) planes of a face-centered cubic spinel LTO (JCPDS card no. 49-0207), respectively. This result indicates that the main phase of all the products is spinel LTO with Fd3m space group. In order to see the trivial effect of the coated material on the LTO crystalline structure, silica fume (JCPDS card no. 27-1402) was used as internal standard to calibrate the systematical error of the XRD analytical equipment. As a consequence, each of XRD profiles demonstrates a set of strong peaks ascribed to Si crystal. All of the XRD curves were then shifted in light of the peak position of Si (111) plane. Correspondently, the detail of the strongest peak representing LTO (111) plane was exhibited in Fig. 1c and d. It is obvious that the central position of this peak

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